



Pergamon

Materials Research Bulletin 35 (2000) 1945–1954

---

---

Materials  
Research  
Bulletin

---

---

## Ultrathin film fabricated from PDDAC/DSB and NDR/DSB

Jinyu Chen, Guobin Luo, Renxiang Wang, Xinsheng Zhao, Weixiao Cao\*

*College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P.R. China*

(Refereed)

Received 20 September 1999; accepted 10 February 2000

---

### Abstract

Two kinds of ultrathin films were successfully fabricated by the self-assembly deposition technique from poly(diallyldimethylammonium chloride) (PDDAC) or nitro-containing diazoresin (NDR) as the polycation and 4,4'-di(sodium styryl-2-sulfonate) biphenyl (DSB) as the dianion. This stepwise fabrication process was monitored by UV-vis spectrometry. The regularity of the film and the morphology of the film surface were examined by X-ray diffraction (XRD) and atom force microscopy (AFM), respectively. The results show that these kinds of films are composed of well-arranged molecules, and have a very flat surface. Among them, the PDDAC/DSB film emits fluorescence when excited with UV light at 354 nm. The NDR/DSB film does not emit fluorescence, because the NDR quenches the fluorescence of DSB; however, the NDR/DSB film possesses more stability against solvent etching (such as DMF), compared with the PDDAC/DSB film. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords:* A. Multilayers; A. Thin films; C. Atomic force microscopy; C. X-ray diffraction

---

### 1. Introduction

Ultrathin films as a kind of advanced material have been attracting more and more researcher attention owing to their various applications such as electroluminescence, photoluminescence, conductivity, and sensor [1–3]. Usually, ultrathin films can be obtained by spin-coating [4], vapor deposition [5], and the Langmuir-Blodgett (L-B)

---

\* Corresponding author. Tel.: +86-10-62751726. Fax: +86-10-62751708.

E-mail address: wxcao@263.net (W. Cao).

technique [6]. Decher and his co-workers [7–10] have developed a novel and simple self-assembly technique for the preparation of ultrathin films, based on ionic electrostatic attraction, which involves alternate deposition on a substrate of two oppositely charged components from their dilute aqueous solutions. Compared with other techniques, especially the L-B technique, self-assembly (SA) is easy to process, friendly to the environment, and inexpensive. Recently, SA has been applied to the preparation of advanced membranes with desired components, such as biomolecules [11], chromophoric molecules [12], dendritic molecules [13–15], polymer dyes [16], and conductive polymers [2]; furthermore, the preparation of stable ultrathin multilayer films has been developed [17,18]. The SA technique also gives us more choices for the preparation of ultrathin films and membranes with desired properties. Li et al. [19] used a complex sequence of substitution reactions on the Si and C atoms to fabricate a dye layer. This is considered to be the earliest work to fabricate better oriented nonlinear films by the self-assembly technique. Katz et al. [20] used a relatively immobile Zr phosphite–phosphate interlayer to connect dye layers, which possesses good orientation. Gao et al. [21] built up an electroluminescent film from PPV/CdSe and found that the nanometer CdSe particles adsorbed on PPV film emit different fluorescence, which changes with voltage. Ferreira et al. [22] fabricated films with high electroconductivity from doped polyaniline or polypyrrole and poly(sodium styrene sulfonate). Recently, Kovtyukhova [23] assembled ultrathin composite films from micro-sized graphite oxide (GO) sheets and polycations and found that GO/polyaniline film shows high conductivity.

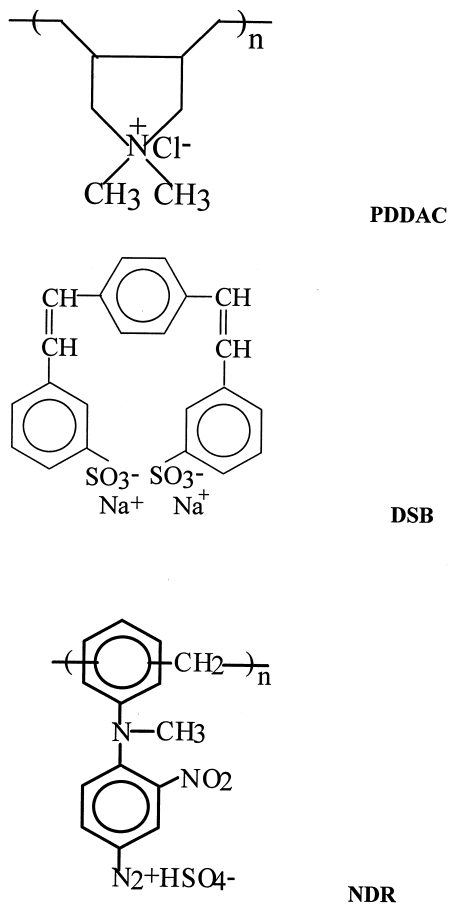
In the present study, PDDAC/DSB and NDR/DSB multilayer films were fabricated using PDDAC or NDR as the polycation and DSB (a fluorescent whitening agent for polyester fiber) as the dianion. The luminescent property, stability toward polar solvents, surface morphology, and regularity of the films were investigated.

## **2. Experimental**

### *2.1. Materials and preparation of multilayer films*

The structural formula of PDDAC, DSB, and NDR are represented in Scheme 1. PDDAC was synthesized according to ref. [24], with  $M_n = 60,000$  g/mol. DSB was prepared according to ref. [25]. NDR was prepared in our laboratory according to a method described elsewhere [26].

The films were prepared at room temperature. Freshly cleaved mica, which has a surface with negative charges in water, was used as substrate. The mica was alternately immersed in the PDDAC or NDR aqueous solution (2 mg/ml) and DSB aqueous solution (2 mg/ml) for 5 min. After each immersion, the mica was rinsed thoroughly with water, and dried. On both sides of the mica, a PDDAC/DSB (or NDR/DSB) bilayer was deposited in each cycle fabrication. The procedure was repeated several times to obtain self-assembly multilayer films.



Scheme 1. Structural formula of PDDAC, DSB, and NDR.

## 2.2. Measurements

### 2.2.1. UV-vis spectrum

A Shimadzu 2100 UV-vis spectrophotometer was used to trace the self-assembly process and the stability of the film. Both DSB and NDR have strong absorption from 300 to 500 nm; therefore, to trace the self-assembly process, the measurement of UV-vis spectra of the film was conducted in this region after every cycle. Using solvent (DMF) to etch the layers of PDDAC/DSB and NDR/DSB films, we evaluated the stability of the film, from the change of UV-vis spectra of the film in this region. To get a flat baseline and reproducible spectra, the micas were cleaved as uniformly as possible. Every measurement was repeated twice.

### 2.2.2. Atom force microscopy (AFM)

AFM was used to visualize the surface morphology of the films. The mica on which the ultrathin film was fabricated was adhered to a glass slide for measurement. AFM measurements were performed with a Nanoscope IIIA (Digital Instruments) in the tapping mode in

air at ambient temperature. Commercial silicon probes (model TESP-100) with typical resonant frequency around 300 kHz were used to obtain the image.

### 2.2.3. X-ray diffraction (XRD)

An RINT 2000 wide-angle goniometer with Cu  $K\alpha_1$  (40 kV, 100 mA) was used to determine the regularity of mica/12  $\times$  (PDDAC/DSB) and mica/12  $\times$  (NDR/DSB) self-assembly films at 20°C. The scan range was from 1.5 to 8°.

### 2.2.4. Fluorescence measurements

An F-4500 fluorescence spectrophotometer (Hitachi Co.) with  $\pm 2$  nm precision and 1.0 nm resolution was used to measure the fluorescence of ultrathin multilayer films at  $\lambda_{\text{ex}} = 354$  nm, which is the characteristic absorption of DSB in ultrathin films.

## 3. Result and discussion

### 3.1. Formation of ultrathin films

It is known that the self-assembled film can be obtained stepwise by alternate deposition of two oppositely charged components on a substrate, usually polyelectrolytes. The mica can dissociate  $K^+$  ions in water to form a negative surface. The polycation is adsorbed on mica via electrostatic attraction. When the mica with a polycation monolayer was immersed into the dianion solution, DSB was adsorbed on the polycations. The procedure was repeated several times to obtain the PDDAC/DSB and NDR/DSB multilayer films. The absorbance of the film vs. the number of bilayers is shown in Fig. 1. The absorbance increases gradually with the number of bilayers, and the inset plot gives the linear relation between the bilayer number and absorbance, both indicating that the fabrication process is indeed stepwise.

The  $\lambda_{\text{max}}$  (354 nm, Fig. 1a) of DSB in PDDAC/DSB film is about 20 nm longer than that of DSB in water (334 nm). The red shift of DSB's adsorption (absorption) in the film may be ascribed to the compact arrangement of the components in the ultrathin film. The wider absorption of NDR/DSB film should be ascribed to the fact that the absorption of NDR tailed over 600 nm and partly overlapped with the absorption of DSB.

### 3.2. Regularity and morphology of self-assembly films

Mica/12  $\times$  (PDDAC/DSB) and mica/12  $\times$  (NDR/DSB) were used for XRD determination. Fig. 2 shows their small-angle XRD diagram. The strong diffraction peaks mean both mica/12  $\times$  (PDDAC/DSB) and mica/12  $\times$  (NDR/DSB) are of good regularity. Using the Bragg equation, the thickness of a bilayer was calculated from the XRD data to be 1.88 nm for PDDAC/DSB and 1.83 nm for NDR/DSB bilayer.

Fig. 3 shows the surface morphology of bare mica (a), mica/1  $\times$  (PDDAC/DSB) (b), and mica/4  $\times$  (PDDAC/DSB) (c) visualized by AFM. From Fig. 3a and b, we can see that most of the surface of sample B was covered with a PDDAC/DSB layer. On the surface of sample C, the PDDAC/DSB was thicker. The mean roughness was determined to be 0.3 nm for bare

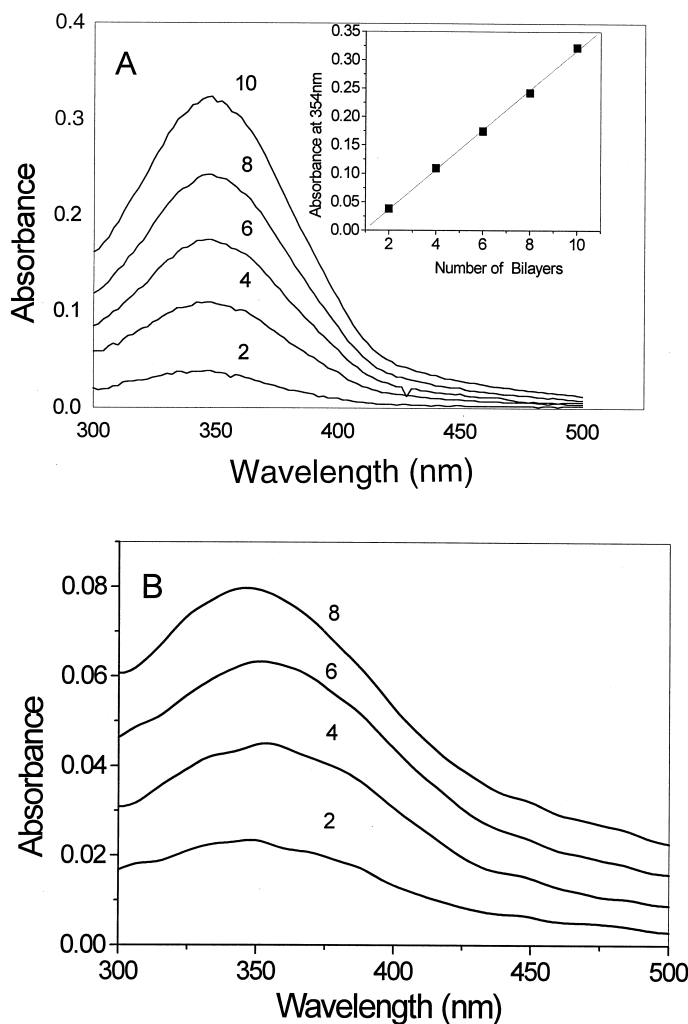


Fig. 1. The absorbance of PDDAC-SB film (A) and NDR/DSB film (B) increasing with the number of bilayers: (A) bilayer number (bottom to top) 2, 4, 6, 8, 10; (B) bilayer number (bottom to top) 2, 4, 6, 8.

mica, 0.8 nm for mica/1  $\times$  (PDDAC/DSB), and 1.1 nm for mica/4  $\times$  (PDDAC/DSB) film in a 2  $\times$  2  $\mu$ m region.

### 3.3. Luminescence of ultrathin films

The PDDAC/DSB ultrathin film emitted strong fluorescence with  $\lambda_{\text{max}}^{\text{F}} = 452$  nm when excited at 354 nm. Furthermore, the fluorescent intensity increased proportionally with the number of bilayers, as shown in Fig. 4. DSB is a good luminescent material and is widely used as a fluorescent whitening agent in polyester fiber. It is interesting that the  $\lambda_{\text{max}}^{\text{F}}$  (452 nm) of the fluorescence in the film was about 7 nm longer than that in water ( $\sim 445$  nm). This may be ascribed to the compact arrangement of DSB in the ultrathin film.

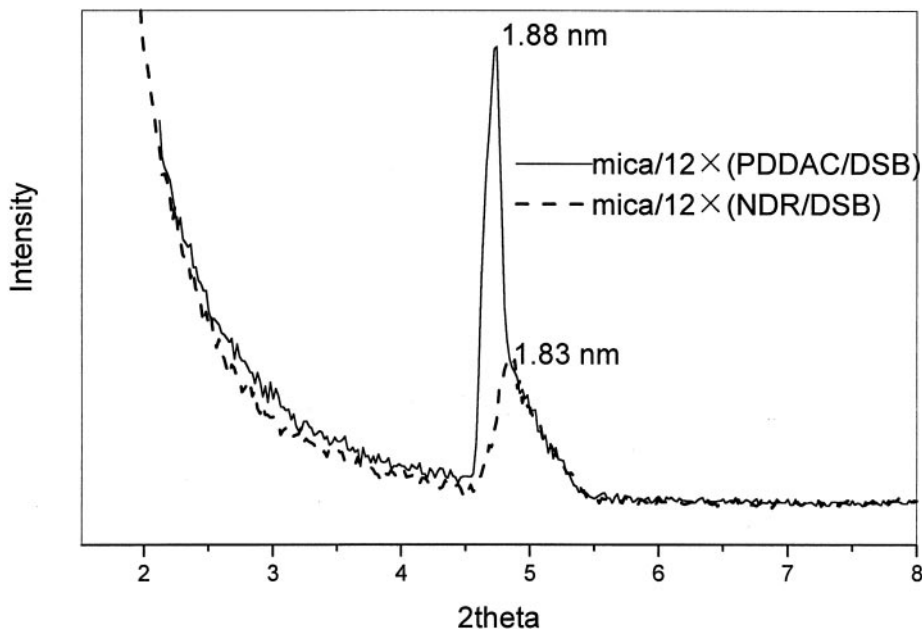


Fig. 2. The XRD diagrams of the 12-layer PDDAC/DSB film and 12-layer NDR/DSB film fabricated on mica.

The linear enhancement of the fluorescent intensity with increasing number of bilayers for the PDDAC/DSB multilayer film (see inset plot of Fig. 4) shows that the fluorescent emission of each bilayer is independent and the overall intensity of the fluorescence of the multilayer film is the summation of bilayer contributions of each bilayer. This is evidence that the fabrication process is carried out in a layer-by-layer manner.

In the case of the NDR/DSB multilayer film, no fluorescence was detected, because DSB's fluorescence had been quenched by NDR. The fluorescence of DSB quenched by NDR in water is shown in Fig. 5.

### 3.4. The stability of NDR/DSB film

NDR/DSB film is photosensitive, i.e., under exposure to UV light (360 nm), the linkage in the film structure changes from ionic to covalent bonds following the decomposition of the  $-N_2^+$  group; the bond nature conversion reaction is shown in Scheme 2. The photoreaction of diazonium salts is relatively complex; however, we believe that the bond conversion from an ionic bond to a covalent bond is dominant, as present in the films fabricated from diazoresin/poly(sodium styrene sulfonate) (NDR/PSS) films [17]. The bond conversion results in an obvious increase in the stability of the NDR/DSB film towards polar solvent. The stability of the NDR/DSB film towards polar solvents increases dramatically because the ionic bond converts to covalent bond in the layers of the film. For instance, about 75% of the film was dissolved after the film was immersed in DMF for 30 min, which can be calculated from the data of absorption at 354 nm. In contrast, the irradiated film (irradiated 10 min at  $230 \mu W/cm^2$ ) was not dissolved even after immersion in DMF for 7 h. Fig. 6 shows the AFM

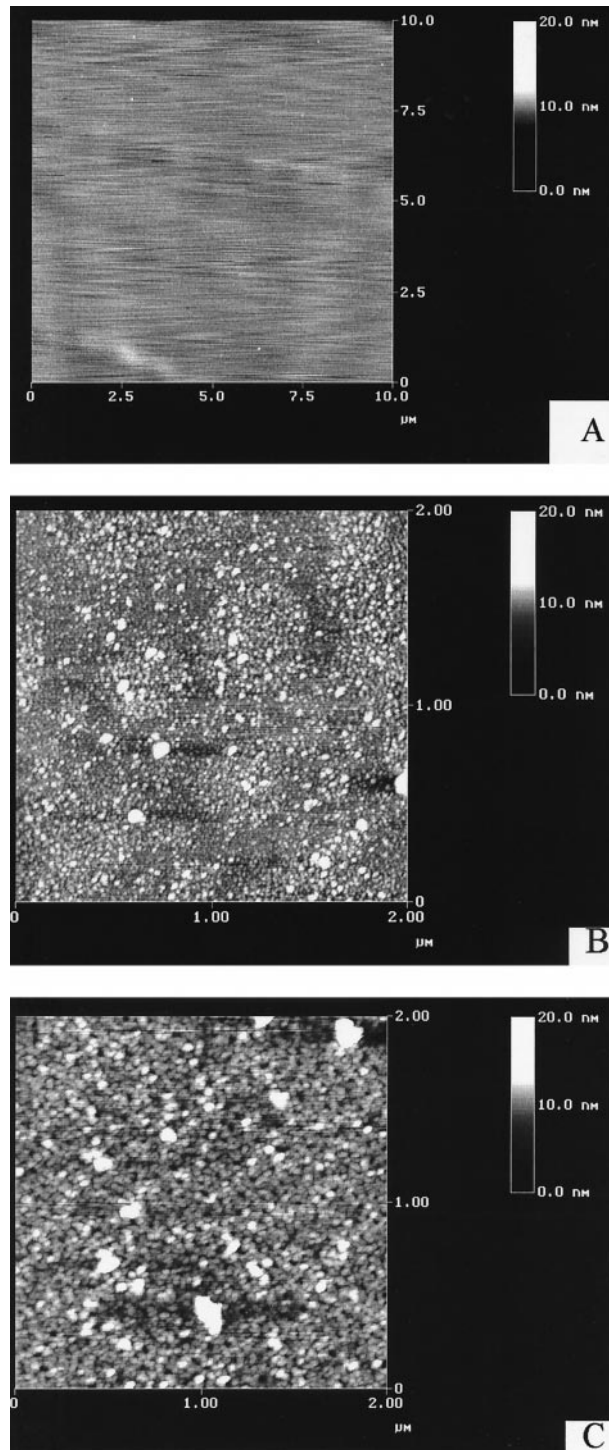


Fig. 3. The AFM images of bare mica (A), mica/1 × (PDDAC/DSB) film (B), and mica/4 × (PDDAC/DSB) film (C).

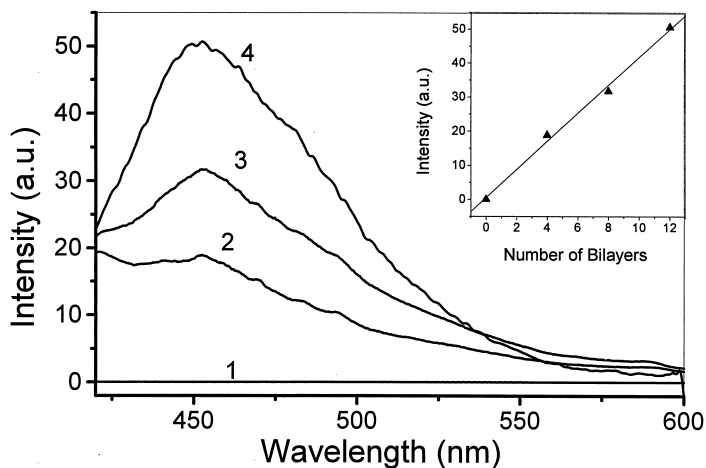


Fig. 4. The fluorescence intensity of PDDAC/DSB film vs. the number of bilayers: (1) 0, (2) 4, (3) 8, and (4) 12.

images of mica/ $8 \times (\text{NDR}/\text{DSB})$  (a) and the irradiated film mica/ $8 \times (\text{NDR}/\text{DSB})$  (b) after immersion in DMF for 2 h. The unirradiated film is nearly completely dissolved, but the irradiated film remains homogeneous. From this, we can see that the irradiated NDR/DSB film is very stable towards polar solvents. This film is obviously different from the PDDAC/DSB film, which is not photosensitive and is not stable towards polar solvents after UV irradiation.

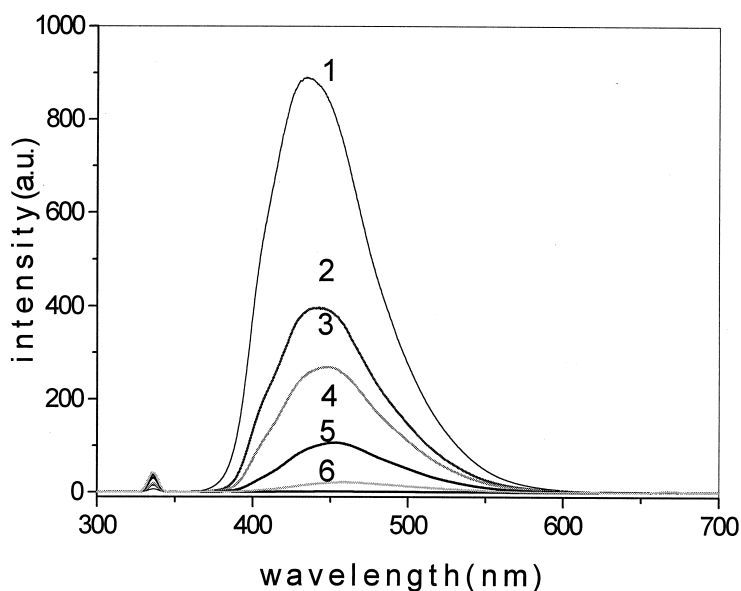
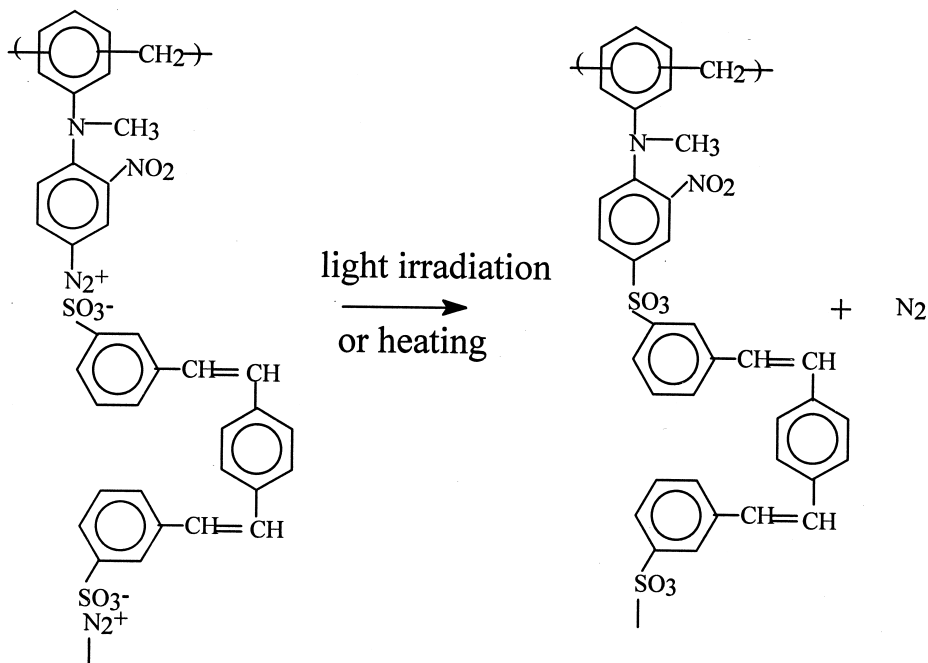


Fig. 5. The fluorescence of DSB quenched by NDR in aqueous solution  $[\text{DSB}] = 5 \times 10^{-4} \text{ M}$ ;  $[\text{NDR}] (\text{M})$ : (1) 0, (2)  $1.5 \times 10^{-5}$ ; (3)  $3.0 \times 10^{-5}$ ; (4)  $4.5 \times 10^{-5}$ ; (5)  $6.0 \times 10^{-5}$ ; and (6)  $7.5 \times 10^{-5}$ .





Scheme 2. The bond conversion in NDR/DSB film under irradiation of UV light or heating.

## Acknowledgments

The authors are grateful to the National Natural Science Foundation of China for financially support of this work (Project No. 59633110, 29874001).

## References

- [1] W. Spevak, J.O. Nagy, D.H. Charych, *Adv Mater* 7 (1995) 85.
- [2] J.H. Fendler, F.C. Meldrum, *Adv Mater* 7 (1995) 607.
- [3] V.V. Tsukruk, *Prog Polym Sci* 22 (1997) 247.
- [4] Y. Lvov, G. Decher, *Crystall Rep* 39 (1994) 696.
- [5] W-K. Wen, J-H. Jou, C-L. Cheng, *Macromolecules* 31 (1998) 6515.
- [6] G. Roberts, *Adv Phys* 34 (1985) 475.
- [7] G. Decher, J.D. Hong, *Makromol Chem Macromol Symp* 46 (1991) 321.
- [8] G. Decher, J.D. Hong, *Ber Bunsen-Ges Phys Chem* 95 (1991) 1430.
- [9] G. Decher, J.D. Hong, J. Schmidt, *Thin Solid Films* 210 (1992) 831.
- [10] M. Losche, J. Schmitt, G. Decher, W.G. Bouwman, K. Kristian, *Macromolecules* 31 (1998) 8893.
- [11] Y. Lvov, K. Ariga, T. Kunitake, *Chem Lett* (1994) 2323.
- [12] A.K. Kakkar, S. Yitzchaik, S.B. Roscoe, F. Kubota, D.S. Allan, T.J. Marks, W. Lin, G.K. Wong, *Langmuir* 9 (1993) 388.
- [13] S. Watanabe, S.L. Regen, *J Am Chem Soc* 116 (1994) 8855.
- [14] V.V. Tsukruk, V.N. Bliznyuk, F. Rinderspacher, *Polym Prepr* 37(2) (1996) 571.
- [15] V.V. Tsukruk, F. Rinderspacher, V.N. Bliznyuk, *Langmuir* 13 (1997) 2171.

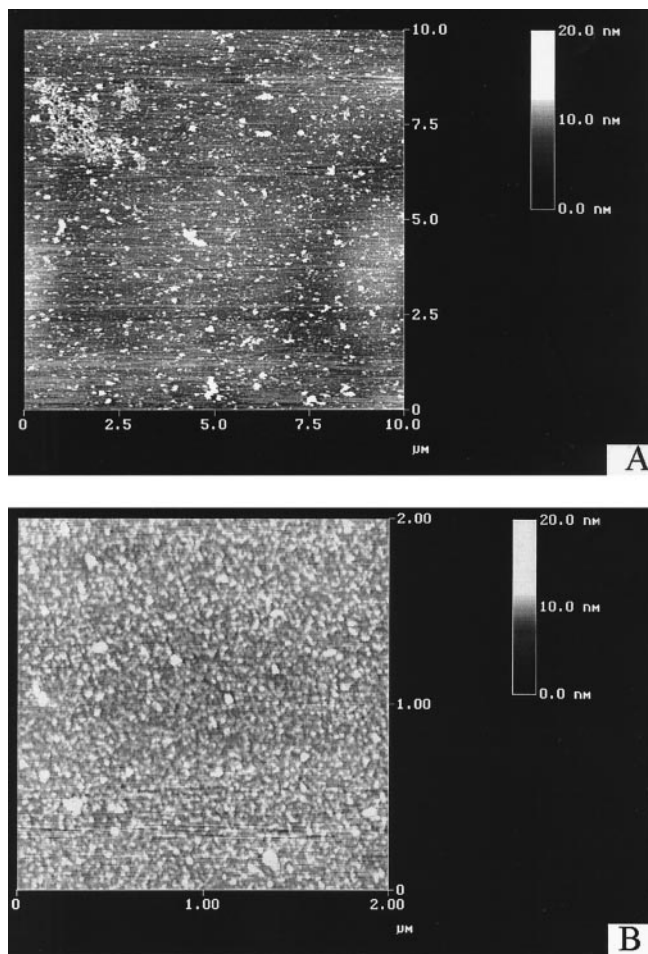


Fig. 6. The AFM images of mica/8  $\times$  (NDR/DSB) (A) and irradiated mica/8  $\times$  (NDR/DSB) (B) after being immersed in DMF for 2 h.

- [16] T.M. Cooper, A.L. Campbell, R.L. Crane, *Langmuir* 11 (1995) 2713.
- [17] J. Sun, T. Wu, Y.P. Sun, Z. Wang, X. Zhang, J. Shen, W. Cao, *Chem Commun* (1998) 1853.
- [18] J. Chen, L. Huang, L. Ying, G. Luo, X. Zhao, W. Cao, *Langmuir* 15 (1999) 7208.
- [19] D. Li, M.A. Ratner, T.J. Marks, C. Zhang, J. Yang, G. Wong, *J Am Chem Soc* 112 (1990) 7389.
- [20] H.E. Katz, G. Scheller, T.M. Putvinski, M.L. Schilling, W.L. Wilson, C.E.D. Chidsey, *Science* 254 (1991) 1485.
- [21] M. Gao, B. Richter, S. Kirstein, *Adv Mater* 9(10) (1997) 802.
- [22] M. Ferreira, J.H. Cheung, M.F. Rubner, *Thin Solid Films* 244 (1994) 806.
- [23] N.I. Kovtyukhova, P.J. Ollivier, B.R. Martin, T.E. Mallouk, S.A. Chizhik, E.V. Buzaneva, A.D. Orchinskiy, *Chem Mater* 11 (1999) 771.
- [24] Y.J. Yang, J.B.F.N. Engberts, *J Org Chem* 56 (1991) 4300.
- [25] G.R. Pettit, B. Green, A.K. Das Gupta, P.A. Whitehouse, J.P. Yardley, *J Org Chem* 35 (1970) 1381.
- [26] R. Wang, J. Chen, W. Cao, *J Appl Polym Sci* 74 (1999) 189.